Amperometric Sensors for Determination of Concentration of Hydrogen Halogenids in Environmental Air

Chvituk V., Linyucheva O., Zaverach E.

National Technical University of Ukraine
Pobeda ave, 37, k.4, Kiev, 03056, Ukraine

The activity of a row of the industrial manufactures of metallurgical, chemical and other industries is accompanied by consumption or production of hydrogen halogenids. Electrochemical sensors can be carried out fast and effective determination of concentration of hydrogen halogenids in environmental air. The difficulties of creation such sensors are caused by specific properties hydrogen halogenids. In particular, in conditions of real humidity of environmental air hydrogen halogenids are inclined to formation of acidic haze and also have high adsorption capability and corrosion activity.

The principle of action the known amperometric sensors of HCl is based on oxidation on a platinum sensitive electrode of ions Cl^- up to Cl_2 or anode dissolution of gold. Alongside with these anode reactions on sensitive electrodes of sensors at their operation and storage the reaction of evolution of oxygen can proceed, that is the basic reason unsatisfactory metrological characteristics of available on the world market sensors of HCl.

We put a task of creation a electrochemical sensor of amperometric type, the principle of which action is based on cathode reaction with participation hydrogen ions - reduction of the oxygen

$$2H^+ + ½\ O_2 + 2e = H_2O \qquad (1)$$

or an oxide of transitive metal

$$(MeO_2)_x(MeOOH)_y + H^+ + e = (MeO_2)_{x-1}(MeOOH)_{y+1}. \qquad (2)$$

Gas diffusion electrodes, which representing porous titanium basis with a coating layer of catalytically active substance - Pt, Au, WC, RuO_2, Co_3O_4 and MnO_2 – are developed.

Kinetic and mechanism of the red-ox reactions in electrochemical cells with the developed gas diffusion catalytically active electrodes in environment of atmospheric air containing an impurity of hydrogen halogenids have been investigated.

Owing to unsufficient convertibility of reaction (1) and change catalytic activity in time the electrochemical cells with Pt and Au sensitive electrodes were characterized by low speed and weak function of the response on change of concentration of hydrogen halogenids. The electrochemical cells with metal oxide sensitive electrodes (RuO_2, Co_3O_4, MnO_2) differ by higher speed and sensitivity in comparison with cells with electrodes from noble metals. The most stable and reproduced operational characteristics are received on cells with MnO_2 electrodes, that is caused by high convertibility of process of solid-state proton-electronic reduction of manganese dioxide (equation 2).

The sensitive element of the developed sensor of hydrogen halogenid contains sensitive gas diffusion manganese dioxide electrode on titanium basis and auxiliary electrode with non-stehiometric manganese dioxide. At short circuit of sensitive and auxiliary electrodes of sensor on loading resistor owing to distinction stehiometric structure of oxide electrodes, and also activity of ions of manganese and H^+ in electrolyte is observed course of a background current, fading in time, that provides constant readiness of the sensor to work.

Under influence a hydrogen halogenid, which diffuse from a gas phase, pH of a electrolyte film in sensitive electrode is reduced, that is accompanied by displacement of equilibrum potential of sensitive electrode in the positive side. But as potential of a electrode answers potential low polarized auxiliary electrode the sensitive electrode will appear cathode polarized and thereof in an external circuit of sensor the current proceeds, which size is determined by the equation

$$I = \frac{E_r - E_{ax.}}{R_s + R_r}, \qquad (3)$$

where E_r -equilibrum potential of sensitive electrode, $E_{ax.}$ - potential auxiliary electrode, R_r - resistance of loading resistor and R_s - internal resistance of sensor. Thus on electrodes of sensor there are connected reactions of reduction of manganese dioxide on sensitive electrode and oxidation of non-stehiometric manganese dioxide in auxiliary electrode according to the equation 2.

The technical characteristics of developed sensors (sensors NTUU) are showed in a table.

Table

The technical characteristics of sensors NTUU

Measuring principle	amperometric two electrode sensor
Minimum and maximum measuring range, ppm	0-10; 0 –100
Sensitivity range, μA/ppm	1,8 – 2,2
Zero current, μA	< 0,3
Equivalent, ppm	< 0,2
Resolution, ppm	0,5
Response time, $\tau_{0,9}$, s	60
Temperature range, ^0C	-20 - +50
Humidity range, %	20 – 95
Sensor life, years	
expectancy	> 3
warranty	1,5
Warm-up time, min	0
Overall dimensions, d×h, mm	26×20
Cross sensitivities to other gases	
NH_3	+
CO	-
H_2S	+
SO_2	-
H_2	-
Cl_2	-

"+"- sensitive; "-" - insensitive

The developed sensors of hydrogen halogenids have passed long field tests on a row of device-making firms successfully, and have found practical application in portable gas analytical devices for determination of concentration of hydrogen halogenids in environmental air.